

# Improving the remarkable photosensitivity of dichromated gelatin for hologram recording in green laser light

Jeff Blyth<sup>a</sup>, Christopher R. Lowe<sup>a</sup>, John F. Pecora<sup>b</sup>

<sup>a</sup> *Institute of Biotechnology, University of Cambridge, Cambridge, CB2 1QT, UK*

<sup>b</sup> *Holograms 3D, 9207 Satyr Hill Road Baltimore, Maryland 21234, USA*

## Abstract

The UV–Visible range absorption spectrum of unexposed dichromated gelatin film (DCG) shows almost no absorption by the dichromate ion at 532 nm. By using a post exposure baking step with a small quantity of glycerol we have managed to produce bright holograms with light energy levels below 50 mJ per cm<sup>2</sup>. This is better than has been achieved with the aid of dyes in DCG and perhaps better than has been achieved so far with any photopolymer system using 532 nm light. Also using 514 nm light from an argon laser, we have achieved a 4 fold increase in photosensitivity over that obtained using conventional procedures. We postulate that this increase in photosensitivity may be the result of an actual amplification of the changes caused by the laser light, and that this effect does not occur in the traditional method using Kodak Rapid Fix plus Hardener. The experimental method detailed here is written with the amateur holographer in mind now that for example powerful green 532 nm cw lasers are readily available at much lower cost. A particular additional feature about the method is the use of potassium dichromate and specifically not the traditional ammonium dichromate.

## 1. Introduction

The large drop in the price of cw lasers emitting at 532 nm over the past 20 years and their general availability caused us to return to some work last carried out by one of us (JB) in 1989 [1]. In that work a useful improvement in photosensitivity was achieved in the quest for recording holograms in DCG using 633 nm red light from a HeNe laser. The system used TMG (tetramethylguanidine) as an electron donor in a methylene blue (MB) initiated system. In this system the light is absorbed by MB and not by the chromate. It now seemed a good time to produce a similar working formulation with a dye for 532 nm. We had assumed that since the natural absorption of dichromate to 532 nm appeared to be virtually negligible (Fig. 1), it seemed obvious that a dye aided system was necessary to overcome that major disadvantage. Preferably the dye needed to be compatible with MB with a view to making the system panchromatic. After we had found such a suitable dye (Safranine 'O') and had started to achieve success with it, the early question of how much better it was than using just the unaided dichromate arose. In spite of its very small degree of absorption at 532 nm there was plenty of evidence from postings and photos on the internet forum hosted by Colin Kaminski [2], that very impressive holographic images were being made by amateur holographers without the aid of any dyes. So the dye sensitization system was put on hold while we went back to basic conventional DCG techniques.

However, we were soon truly amazed to find that through rationalizing on basic principles established over more than 3 decades, we could not only beat the photosensitivity of the dye system to 532 nm but also achieve an improvement in photosensitivity by a factor of at least 3 on the current conventional DCG system.

## 2. Results

Fig. 2 shows a picture of 2 holograms of fingers holding a coin. The image on the right was made with a single 6 ns pulse of 532 nm light and the one on the left was a 1 second burst of about 10 pulses. Clearly the single pulse exposure on the right was underexposed while the multiple-pulse image on the left was overexposed. Using a Fieldmaster meter set-up for pulsed lasers from Coherent Inc., the energy used to make that single pulse image of living fingers was apparently as low as 12 mJ per cm<sup>2</sup>. In spite of being underexposed it is remarkable to have been able to record anything at all at 532 nm with that level of energy. Using a continuous wave 20 mW 532 nm laser pointer, bright holograms of diffusing objects with energy levels of about 40 mJ per cm<sup>2</sup> were made. This was slightly better than we were achieving with the dye chromate system.

One of us (JFP) then used the system with his 514 nm argon laser.

Fig. 3 shows a photo of the model castle ( $2\frac{1}{4} \times 3$  in.) used to make the hologram on the right with exposure energy of 25 mJ/cm<sup>2</sup>. Bright holograms were obtained with 514 nm

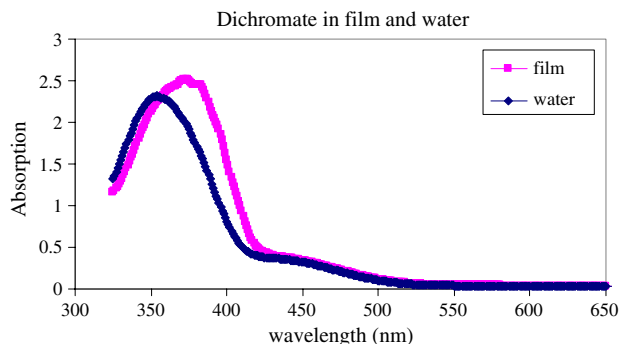


Fig. 1. The absorption spectrum of dried unexposed gelatin film that had been soaked in 5% potassium dichromate is shown with the spectrum of 5% dichromate in water (in the form of a very thin film in a glass sandwich).

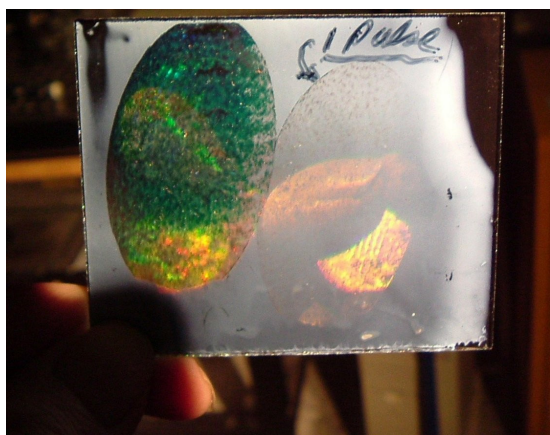


Fig. 2. The right hand image of fingers holding a coin was made with a single 6 ns pulse of 532 nm light from a YAG laser; with an energy level of only about  $12 \text{ mJ/cm}^2$  it is clearly underexposed but nevertheless quite remarkably visible. The left hand image is made from about 10 such pulses spread over 1 s and is certainly overexposed.

energy levels from  $30 \text{ mJ per cm}^2$  down to the dimmest images around  $5 \text{ mJ per cm}^2$ .

### 3. The method

The brief overview of the steps we finally used in our system are as follows:

- (1) Coat gelatin onto glass.
- (2) Immerse the dry film in a solution containing potassium dichromate and glycerol.
- (3) Expose to 532 nm or 514 nm laser light.
- (4) Thermally encourage completion of the light induced dichromate transition to CrIII at  $100^\circ\text{C}$ . Typical baking time is between 2 and 5 min.
- (5) Immerse the cool plate in a stirred water bath with controlled temperature.
- (6) Then to use a sequence of 3 iso-propyl alcohol baths at room temperature but using the simple cover plate technique advocated by Bahuguna et al [3].
- (7) Then to put the finished plate back in the oven at  $100^\circ\text{C}$  to completely dry out.



Fig. 3. Using  $25 \text{ mJ/cm}^2$  of 514 nm light from an argon laser (with etalon) the hologram of a model castle [ $2\frac{1}{4} \times 3 \text{ in.}$ ] is shown on the right with picture from the manufacturer's catalogue on the left. (Exposure time 50 s.)

### 4. Gelatin coating on glass

The gelatin coating can be done following a number of sources.

Particularly helpful is the discussion and video clip from D. Battin on the above mentioned holography forum [4].

We chose however to use the Meyer bar coating method because it was available to us.

A narrow 2.5 mm thick glass sheet, 150 mm wide and about 990 mm long was treated overnight in a bath of 5% tri-sodium phosphate (TSP). This caustic solution was then washed off in de-ionized water. This treatment helps the gelatin to key onto the glass. Ordinary undiluted household bleach may also work well. The glass is then laid along a levelled horizontal board which was a half cm less wide than the glass. Sticky tape was then run down both sides of the board so that it just adhered to the underside of the  $\frac{1}{4} \text{ cm}$  overhang of the glass sheet on each side. This prevented the gelatin solution from creeping onto the back of the glass.

#### 4.1. Gelatin formulation

In our system we used a high bloom strength gelatin, [260 bloom "limed ossein" from Croda Colloids].

0.3 g glycerol was first added to a glass beaker followed by 100 ml de-ionized water and a magnetic follower.

12 g of gelatin granules were then vigorously stirred in to the cold solution on a magnetic stirrer hotplate.

The solution in the beaker was then heated in a non-magnetic metal water bath and the temperature of the solution was monitored and kept to within  $50$  to  $60^\circ\text{C}$  for about 40 min then finally 1.0 ml of a 5% potassium dichromate solution was stirred in. (This 5% dichromate solution will be used later to photosensitize the coating.) It was then filtered through nylon mesh into a fresh beaker which was then kept at about  $60^\circ\text{C}$  while the glass sheet was warmed with a hot hairdrier.

The Meyer bar,  $\sim 7$  windings per cm, length 30 cm, diam. 1 cm, warmed in hot water, dried and placed at the far end of the sheet and a puddle of the gelatin solution was made on the glass across the width and extending nearly half way down the sheet. The Meyer bar was then drawn down the sheet at a steady constant rate. (The draw down took about 15 s.)

**Notes.** *The problem of coating gelatin solutions with hardeners is that they rapidly increase the viscosity of the solution and commonly cause gelling before the coating operation is completed. The approach which appealed to us in the latter stage of this project was to return to one of the original ideas from the early work at Bell Telephone Labs [5]. Namely this was to include in the gelatin solution a very low concentration of a "potential hardener" which could be activated later. The simplest practical answer was indeed to use ammonium or potassium dichromate. So the gelatin solution is prepared but then finally, just 0.5% of dichromate (based on the weight of dry gelatin) is stirred in. Either the ammonium or potassium salt is OK here. It should be emphasized that this initial use of a very small quantity of dichromate should be viewed quite differently from the necessarily high concentration of dichromate needed to make the holograms later. Our use of glycerol at this point acts as both a plasticizer and catalyses thermal hardening if required at this point. The coating is then carried out but to ease the clean up operation later it is best done under subdued lighting. The great advantage of not coating the gelatin down with all the high concentration of dichromate present for full photo-sensitization is that then the troublesome limited lifetime of unexposed sheets with their constantly increasing hardness from a dark reaction is avoided. Also the coating does not need to be done under red safelighting. Sheets can be stored indefinitely without refrigeration and can be used to make consistent freshly sensitized plates as needed.*

Once dried in cool air-flow the coating can either be lightly hardened by leaving it in direct sunshine for at least 20 min or left in ambient daylight for a day or two. Alternatively because the formulation contains glycerol, the gelatin can be hardened in an oven at around 100 °C for about 20 min (which is more convenient than 2 h at 150 °C recommended in the original 1969 paper [5]). The glass sheet is then cut up into conveniently sized plates.

## 5. Photosensitization method

### 5.1. Photosensitizing solution

0.5 g glycerol

100 ml de-ionized water

5 g potassium dichromate (note, ammonium dichromate is NOT an alternative)

about 5 drops of photographic wetting agent

Under red (not yellow) safelighting, the plate is immersed in cold photosensitizer ( $\sim 10$  °C) for about 40 s then the liquid is wiped off the back and the plate stood up to dry with its base resting on blotting paper.

If there are any droplets remaining on the gelatin surface at this point then more surfactant is needed. One can very gently run a soft rubber wiper blade over the surface to remove droplets. Plates are then left in a good unheated air flow until touch dry.

**Note.** *If green objects still look green under the safelight then the safelight is not safe. One can use the diffraction effect from the surface of an ordinary CD to check that there is no significant green or blue from the safelight.*

## 6. Thermal hardening method

A clean very flat and preferably thick metal plate needs to be arranged in an internally unlit oven at 100 °C.

Another clean flat metal plate needs to be positioned next to the oven under safelighting.

After the laser exposure, we placed our plate face up on the 100 °C metal plate. And left it there for a bake time which had been found by trial and error tests. The bake time is quickly brought to an end by removing the plate and placing it face down on the cool flat metal plate outside the oven. On 2 mm thick glass the optimum bake time could be 2 min and on 3 mm glass the optimum bake time might be  $\sim 4$  min.

## 7. Wet processing

We found it convenient to use glass or plastic beakers as baths that allowed plates to stand up at an angle of about 45° with the emulsion facing down so that a short magnetic stirrer bar could give good agitation of liquid across the gelatin surface.

Our first bath was typically water at 25 °C. The exact temperature had to be found by trial and error. The appropriateness of a chosen temperature could only be judged after the hologram had been fully processed in the subsequent baths. The cool holographic plate was placed in the rapidly agitated water bath and at this point safelighting was no longer necessary. After about 1 min, a cover plate the same size as the holographic plate was slid into the bath so that it covered the gelatin surface. The glass sandwich was then withdrawn and the water droplets wiped off. The sandwich was then placed (with the cover plate down facing the stirrer bar) in a well stirred bath of roughly 60% iso-propyl alcohol (ipa) at room temperature. The sandwich was then opened and the cover plate was removed from the bath while the gelatin coating was left to equilibrate for about a minute, then the cover plate was slid back into the bath and the sandwich reformed before transferring to a second alcohol bath at room temperature which had not been initially diluted (but after a few plates had passed through it was no longer "100%" ipa). The cover plate was then removed under the liquid of the second alcohol bath as before and the stirring continued for about 2 min. Finally the hologram was transferred to a 3rd bath of 100% ipa for at least 2 min.

Plate was then given a brief strong blast of hot air from a blower (to prevent droplets of ipa being placed in the oven) and then again placed in the oven face up on the 100 °C metal plate to dry out completely for at least 5 min.



**Notes.** We found the simple cover plate technique advocated by Bahuguna et al [3] helped greatly to avoid blotches from uneven processing. This particularly applies to the transfer from the water bath to the first alcohol bath. Water droplets and rivulets can cause unequally strained areas and then there is the point that the plate is taken out of a water bath whose temperature is close to the critical level above which the milkiness effect will be created in the finished hologram. Even with ipa at only 60% concentration the heat generated by meeting water might be enough to surpass the critical temperature level. (A mouthful of good brandy (~45% alcohol) testifies to this heating effect!).

For doing several plates sequentially it is important to use fresh water each time to avoid any significant amounts of glycerol and chromium salts getting into the alcohol bath and leading to eventual increased susceptibility to humidity in the finished hologram.

## 8. Discussion

It is nearly 40 years since the first pioneering papers on holographic recording of images in DCG appeared from the Bell Telephone Labs. In the first paper Shankoff [6] did use the 514 nm from an argon laser as well as the much more effective 488 nm. It was only a few months later that Lin in a strikingly pragmatic paper [7] put forward the idea of employing the product Kodak Rapid Fixer with Hardener to harden the gelatin before exposure and to treat the film after the exposure. The use of this product after the exposure step has become the conventional method. According to Kodak's product safety sheets, part A consists mainly of ammonium thiosulfate and part B consists mainly of aluminum sulfate (alum). For over 30 years it has become almost routine in the literature on holography using DCG to comment on the difficulty of understanding what is happening in the post-exposure treatment baths and yet there has been little attempt to question the wisdom of simultaneously using a proprietary fix and hardener designed only for use in photographic processing. These cheaply available chemicals should have been tested independently to find out what they were actually doing. We have no doubt that this has held back the understanding of the holographic fringe development process in DCG. One of us (JFP), after much experience in producing very bright holograms by the conventional method, was quite surprised to discover only recently that leaving out the fixer had a far more detrimental effect than leaving out the hardener (alum). He had until then assumed like most users that the hardener was the most important constituent. The importance of the fix rather than the hardener is offering us a valuable insight into the primary process. Kodak lists the constituents of part A as:

40–45% water; 42% ammonium thiosulfate; 5–10% sodium acetate; 1–5% boric acid; 1–5% ammonium sulfite; 1–5% acetic acid; <1% sodium bisulfite.

Our belief is that it is the sulfite and bisulfite ions that are of great consequence and the actual thiosulfate “fix” is

superfluous to our requirements in DCG. The reasoning is as follows.

Exposing dichromate-gelatin is known to cause the dichromate to be finally reduced to chromium III and this product is primarily responsible for the crosslinking and insolubilization of the gelatin. Some of the gelatin must also become oxidised by the dichromate but this has not been found to contribute to its insolubilization [8]. It has long been realised that after exposure much of the crosslinking occurs at room temperature in the dark over several hours and workers a century ago making photographic prints discovered that there was a slow increase in electrical resistivity over this period [8]. Recent work has shown that during exposure a gelatin-Cr(V) species is instantly produced and that this species has been tracked by ESR measurements and shown to be capable of lasting for many hours at room temperature before finishing up as Cr(III) [9].

From these facts we can form the reasonable assumption that the holographic exposure initially produces in the light-struck fringes a transformation of Cr(VI) to a Cr(V) form which must be necessarily bound to the gelatin matrix—otherwise the moment it was immersed in water it would migrate away and the future integrity of the fringe structure as defined by the future formation of Cr(III) crosslinks would be gone. Meanwhile the dark fringes must still contain chromium which is still virtually all in the Cr(VI) state and once immersed in water this chromium is free to migrate away. Now here perhaps lies a key point. We conjecture that unless that Cr(VI) does manage to leave its sites within the dark fringe it could be reduced there by the strong reducing agent bisulfite/sulfite and become indistinguishable from the Cr(III) in the neighbouring light fringes. So the fringe contrast would be lost (except for the relatively small amount of oxidized gelatin exclusively in the light fringes).

So, to now maximize the fringe differences in the wet step using the Kodak Fix, what is required is for the light induced and immobilized Cr(V) species to be much more quickly reduced by the sulfite ions than the unbound Cr(VI) species in the adjacent dark fringes. We can assume that this situation is helped by the probability that any Cr(V) intermediate produced in the dark fringe would not be bound to the gelatin as it is not produced by the oxidation of the gelatin but by the oxidation of sulfite ion. This would mean that until the Cr(VI) in the dark fringe is reduced down to Cr(III) it will not bind to the gelatin. On this point it has been shown that the speed of the reaction between gelatin and Cr(III) is not slow [9]. If we were only to consider fringes on the surface, then strong agitation of the water bath would be a positive step to wash away the high concentration of Cr(VI) in the dark fringes, but in the case of reflection fringes buried in the volume of the gelatin, agitation can only be of limited benefit, and what is important is the osmotic pressure difference between the high ionic strength from the chromium ions inside the layer and the solution outside. This difference is bound to rapidly eliminate a lot of the free Cr ions from the gelatin. So one may now ask what the purpose of adding Kodak's alum hardener to that first bath is.

**Table 1**

Approx. solubilities of dichromate salts in grams per 100 ml (from various sources)

| Dichromate         | Mol. wt. | 80 °C | 20 °C | 15 °C | 0 °C |
|--------------------|----------|-------|-------|-------|------|
| Ammonium           | 252.1    | —     | 37    | 31    | —    |
| Potassium          | 294.2    | 80    | 12    | 8     | 5    |
| Sodium (anhydrous) | 262.0    | 447   | 236   | —     | 209  |

$\text{Al}^{3+}$  ions will increase the overall hardness bias requiring a higher processing temperature to maximise fringe contrast. A freshly coated DCG layer can be too soft in its dark fringe area to maintain good fringe integrity. So, a certain minimal level of hardness is necessary.

## 9. The extraordinary photosensitivity to green wavelengths

There would seem to be two questions here. (1) Why is there 532 nm photosensitivity when the absorption spectrum in Fig. 1 suggests otherwise? and (2) how is this sensitivity so enhanced by the post exposure thermal hardening method compared to the wet traditional Kodak Rapid Fix method? This question will be discussed in the thermal hardening method paragraph below.

The answer to the first question must be that we are compensating for the very low absorption by using a very high concentration of dichromate compared to the typical concentrations of dyes used in dye-initiated photo systems. However when high concentrations of dichromate are used with wavelengths in the blue or violet region then the much stronger absorptions there can cause problems by absorbing too much object light to make a good single beam Denisyuk reflection hologram and also it causes significant intensity gradients within the thickness of the gelatin layer and this leads to hardness gradients and broadband replay effects (McGrew) [10]. With such low absorption values in the green region, one would expect that the higher the concentration of dichromate the better the photosensitivity. Therefore, from Table 1 one would expect that the best available salt to use would be sodium dichromate. However, we tried this and found that sodium dichromate-sensitized coatings were quite dead and useless within a very few hours. Apparently the relatively large amount of transition metal impurity in the sodium compound greatly speeds up the dark reaction which is well known to be speeded up by traces of copper, cobalt and nickel in particular [8]. It is the very high solubility of the sodium compound that makes it difficult to purify. This also emphasizes that purer dichromate grades should be used to minimize the dark reaction rate.

### 9.1. Thermal hardening method

The small amount of glycerol in our sensitizer formulation appears to play a crucial role in enabling the transformation of the light-produced Cr(V) to take place much more rapidly at 100 °C. Without glycerol the process seems to take more than a half hour to harden sufficiently. So it may be true to

say that hot glycerol catalyses the reaction  $\text{Cr(V)} \rightarrow \text{Cr(III)}$ . The reason we cannot use ammonium dichromate is because the ammonium salt decomposes at elevated temperatures into free ammonia gas and the extremely reactive compound chromic acid. This rapidly reacting compound will be formed in the dark fringes and harden them, whereas our goal is to specifically harden the light fringes by converting just the exposure-produced Cr(V) leaving the Cr(VI) in the dark fringes unaffected in the short term. Using ammonium dichromate in practice leads to violet-black images.

Is the 3 or 4 fold increase in photosensitivity in the thermal method over the Kodak Fix-Hardener method due to the latter suffering from some form of inefficiency or could it possibly be due to an actual amplification effect achieved only in the thermal method with the help of hot glycerol? We hypothesize that the answer could be due to the latter, the reasoning is as follows. It is established that the dark reaction can be much accelerated by transition metal ions with their variable oxidation states promoting catalytic effects leading to the dark breakdown of dichromate Cr(VI) [8]. We propose that there is still much unconverted Cr(VI) in the correctly exposed light fringes (and obviously more still if light fringes are underexposed). What if the Cr(V) compound in the light fringes when taken to 100 °C with hot glycerol present, acts as a catalyst breaking down more Cr(VI) with which it is in contact? The net result of this would be that more Cr(III) is finally formed in the light fringes than would be formed by just the Cr(V) alone transforming to Cr(III), i.e. Cr(V) in hot glycerol infects more Cr(VI) and induces its break down—this then qualifies as an amplification effect.

Whereas with the Kodak-Fixer wet method, all the unconverted Cr(VI) in both dark and light fringes will immediately migrate away into the solution and quickly be converted into lower oxidation states, while the more reactive but immobilized Cr(V) species is being rapidly reduced to Cr(III) thus crosslinking the gelatin. So no amplification effect occurs because there is no additional amount of Cr(III) produced within the light fringes as a direct result of the original light energy.

## 10. Conclusion

More than a 3 fold increase in the photosensitivity of DCG to the green wavelengths has been achieved by substituting the traditional Kodak Rapid Fix hardener system with a thermal hardening system in the presence of glycerol and also by the substitution of ammonium dichromate by potassium dichromate.

We have not introduced anything radically new here, a post-exposure 100 °C thermal treatment has been advocated for dichromated gelatin plates manufactured by Slavich [11] for some while but the required bake time there can be as long as an hour and the photosensitivity seems to be lower than we are achieving. The use of glycerol or other glycols has been patented for a “self-developing” DCG system with good photosensitivity which avoids the need for wet processing [12,13] but apparently the finished product there

has a very short useful lifetime and may be unsuitable for display holography.

So, we seem to have managed to have made an advance in DCG display holography simply by going back to basics.

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